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# **Ultrasound promoted reaction of Rhodamine B with Sodium Hypochlorite using sonochemical and dental ultrasonic instruments**

T. Joyce Tiong and Gareth J. Price\*

Department of Chemistry, University of Bath, BATH, BA2 7AY, UK.

E-mail: [chsgjp@bath.ac.uk](mailto:chsgjp@bath.ac.uk)

## **Abstract**

The sonochemical acceleration of bleaching of Rhodamine B by sodium hypochlorite has been studied using ultrasound intensities in the range  $0 - 7 \text{ W cm}^{-2}$ . Using a 20 kHz ultrasonic horn, it was shown that ultrasound could significantly shorten the treatment time and/or the concentration of hypochlorite required for the reaction. A number of intermediate species formed during the reaction have been identified. It was demonstrated that the same sonochemical reactions occur during the use of dental ultrasound instruments of the type used in endodontics where hypochlorite solutions act as disinfectants. Results showed pseudo-first order degradation kinetics for the degradation of Rhodamine B for both types of source. Both the distribution of cavitation and the resulting bleaching reactions were dependent on the design of the tips. The bleaching reaction can therefore be used to characterise the behaviour of dental instruments and aid in the optimisation of their performance.

*Key words:* hypochlorite, endodontics, dye, bleaching, dental ultrasound

## 1. Introduction

In addition to applications in chemistry and chemical processing, high power ultrasound has found a range of uses in medicine and dentistry. In the latter, perhaps the most common application is in descalers where metal tips vibrating at 20 – 40 kHz are used to remove plaque and other deposits from around teeth and gums [1, 2]. It has recently been shown that cavitation can be produced around dental descalers. [3] The detailed shape and design of the tip influenced the amount of cavitation produced and its spatial distribution. [4, 5] Another widespread application of ultrasonic instruments is in root canal surgery - known as endodontics [6, 7]. Here, infected tissue must be removed from deep inside the tooth and this is assisted by the vibratory motion of the instrument which aids dissolution and dislodgement of material [8] which is carried away by an irrigant fluid. Use of a disinfectant in the irrigant also serves to sterilise, at least in part, the tooth root to assist in preventing future infection [9], sodium hypochlorite, NaOCl, often being used [10] since it is a strong oxidising agent and also kills bacteria. [11]

Many of the clinically useful effects of ultrasonic dental instruments either arise from or can be enhanced by cavitation. The same is true for the chemical effects of ultrasound. It is therefore of interest to compare the effects produced by these dental instruments with more conventional sonochemical sources of ultrasound.

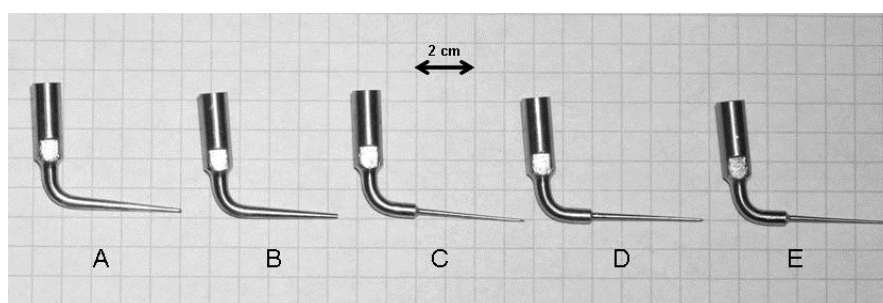
A number of workers have applied ultrasound to enhance the bleaching and disinfectant properties of NaOCl. Blume and Neis [12] showed that 20 kHz ultrasonic treatment led to shorter treatment times with lower doses during wastewater disinfection with chlorine. Duckhouse and co-workers [13] applied ultrasound at 20 and 850 kHz to water contaminated with E-coli and found benefit to the disinfection efficiency of NaOCl while Joyce *et al.* [14] applied ultrasound during in situ electrolytic production of NaOCl from saline solution combined with UV irradiation. A large number of studies of the use of ultrasound to treat waste water containing dyestuffs have been published. Several of these have involved combination with hypochlorite to achieve high rates and efficiencies. For example, Pizzolato and co-workers applied this system to waste water from a mineral plant [15] and found that a wide range of compounds could be decolourised in a few minutes treatment while Gogate *et al.* [16] used a pilot scale reactor to investigate sonochemically enhanced bleaching using Rhodamine B as a model dye. The same dye has been used by a number of workers as a model system [17, 18].

Given the widespread use of Rhodamine B, its bleaching by hypochlorite has been used in this work to characterise the effect of ultrasound on the reaction using a high power sonochemical horn system and the results compared with measurements using an endodontic dental system with tips of different shapes and sizes.

## 2. Experimental

All reagents were analytical grade, obtained from Sigma-Aldrich Co., UK, unless otherwise stated and were used as received. Sodium hypochlorite solutions were prepared by dilution of the commercial product (13% w/v active chlorine (Acros Organics)); concentrations are reported as % w/v. Rhodamine B solutions of  $5 \text{ mg L}^{-1}$  were used, changes in concentration being monitored by measuring the absorbance at 554 nm on an Agilent 8453 UV-visible spectrometer. Measurements of HOCl concentrations were performed using the method of Morris [31] employing UV-vis spectroscopy at wavelength of 290 nm.

Sonication at 23 kHz was carried out with a Sonics & Materials VC 600 fitted with a 1 cm diameter titanium-alloy horn.  $100 \text{ cm}^3$  of the solution under investigation was measured into a beaker fitted with a water jacket to regulate the temperature. The results reported here were recorded at  $20 \pm 4 \text{ }^\circ\text{C}$ . A Piezon miniMaster provided by Electro Medical Systems, Nyon, Switzerland was used as the dental source. This consists of a piezoelectric transducer held in a handpiece into which a tip is fitted. The five different tip designs (each is ca. 15 to 20 mm in length) used are shown in Figure 1. The unit operates at a nominal frequency of 30 kHz, and can be set to any of ten incremental power settings from a control panel. For this work, power settings of 1/10, 5/10 and 10/10 were used. The tip was immersed in  $3 \text{ cm}^3$  of  $5 \text{ mg L}^{-1}$  Rhodamine B solution contained in a quartz cell. The intensity of ultrasound was measured calorimetrically in the usual manner [19], by calculating the heat dissipated into a known amount of water and dividing by the surface area of the tip. Control experiments were performed on an IKAMAG hot plate with controlled stirring rates.



**Figure 1.** Endodontic tip designs

Liquid chromatography coupled with mass spectrometry (LC-MS) was performed to identify the degradation products formed upon sonication using a Daltonics micrOTOF electrospray time-of-flight (ESI-TOF) mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) coupled to an Agilent 1200 LC system (Agilent Technologies, Waldbronn, Germany). 10  $\mu\text{L}$  of sample was injected into a 30:70 flow of water:acetonitrile at 0.3 mL/min. 10  $\mu\text{L}$  of 5 mM sodium formate was injected after the sample as a calibrant over the mass range  $m/Z = 50\text{--}1500$ .

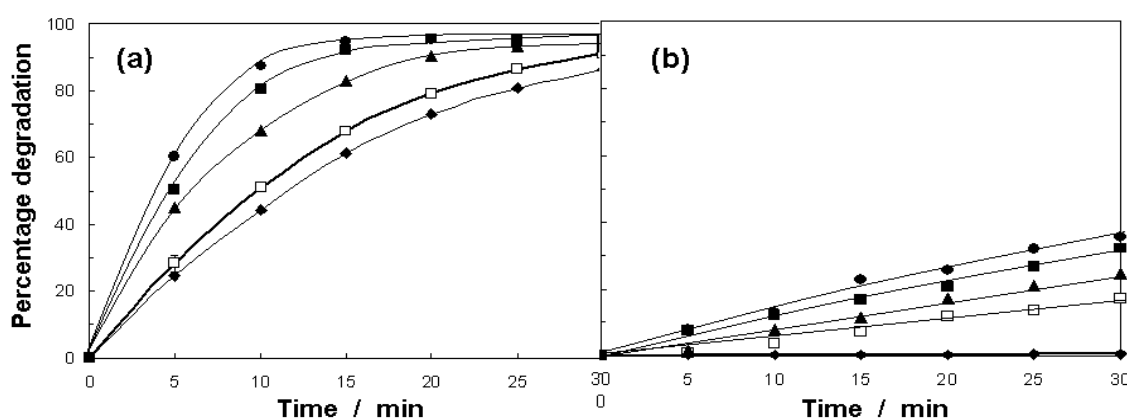
In order to record sonoluminescence images, the apparatus was contained in a light-proof box. Images were recorded for 30 s with the dental tips operating in a solution of chemiluminescent luminol [20]. This was prepared by dissolving 1 mmol of luminol (3-aminophthalhydrazide, 97%), 0.1 mol hydrogen peroxide and 0.1 mol EDTA (ethylenediaminetetraacetic acid) in 1  $\text{dm}^3$  of 0.1 M sodium carbonate. The solution was adjusted to pH 12 by adding sodium hydroxide. Images were recorded on a digital single-lens reflex camera (Nikon D60) body, using a macro lens of 60 mm focal length at an aperture of f2.8, focusing the dental instrument in order to obtain a 1:1 image ratio. The camera has an imaging resolution of  $3872 \times 2592$  pixels (10.0 megapixels). The total intensity of the emission was calculated after subtraction of background levels using ImageJ software [21] which was also used for further image manipulation over a fixed region of interest.

### 3 Results and Discussion

#### 3.1 Sonochemistry system

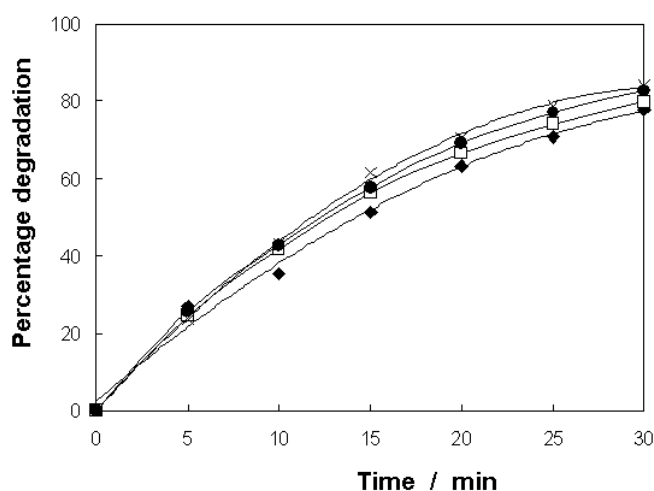
Figure 2(a) shows the effect of ultrasound from a 23 kHz sonochemical horn system on the bleaching of Rhodamine B by a 2% hypochlorite solution. The initial concentration of dye was  $5 \text{ mg L}^{-1}$  ( $ca. 1 \times 10^{-5} \text{ mol dm}^{-3}$ ). Control experiments in the absence of ultrasound were performed with different stirring speeds with the results shown in Figure 3. An increase in stirring speed accelerates the degradation process slightly, although the difference is less than 8% between the slowest (200 rpm) and the highest (800 rpm) stirring speeds used. On the other hand, the much greater acceleration promoted by ultrasound is clear. In the absence of ultrasound 50% of the dye absorbance is lost in *ca.* 10 min, whereas only 4 min is needed when using  $6.7 \text{ W cm}^{-2}$  ultrasound. As expected, higher intensities lead to a faster reaction although the rate of reaction at the lowest intensity is slightly slower than the silent reaction (i.e. in the absence of ultrasound). This may be due to the lowest intensity being at or below the cavitation threshold or that the mixing is less effective than the stirring used for the silent reaction so that the rate is reduced.

There are several reports of the degradation of Rhodamine B using ultrasound both in the presence and absence of additional oxidising agents. [16, 22, 23] The results of degradation of Rhodamine B using ultrasound alone are shown in Figure 2(b). Significant degradation is observed but it is much slower than when in the presence of hypochlorite. This degradation proceeds largely as a result of reaction with hydroxyl radicals and subsequent formation of hydrogen peroxide formed as a result of water sonolysis. Given the structure and, in solution, ionic nature of Rhodamine B (see Scheme 2), it is unlikely that it will enter the cavitation bubble to undergo pyrolysis and so a degradation process in solution will be favoured. [24] This is also supported by the product analysis discussed below.



**Figure 2.** Effect of ultrasound intensity on the bleaching of 5 mg L<sup>-1</sup> Rhodamine B (a) with 2% sodium hypochlorite (b) no NaOCl. (Uncertainties in the percentage degradation are  $\pm 3\%$ )

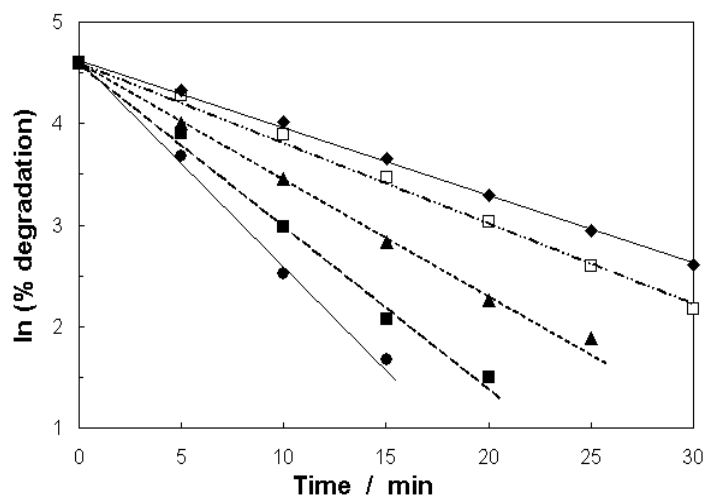
Ultrasound intensity / W cm<sup>-2</sup>: □ 0 (no ultrasound) ◆ 1.5 ▲ 3.0 ■ 4.6 ● 6.7



**Figure 3.** Degradation of 5 mg L<sup>-1</sup> Rhodamine B with 2% sodium hypochlorite at different stirring speeds. (Uncertainties in the percentage degradation are  $\pm 3\%$ )

◆ 200 rpm □ 400 rpm ● 600 rpm × 800 rpm

Given the relative concentrations of NaOCl and dye, the former is in vast excess so that a *pseudo*-first order reaction might be expected. This is indeed observed as shown in Figure 4 which also allows calculation of the rate constants for the reaction.



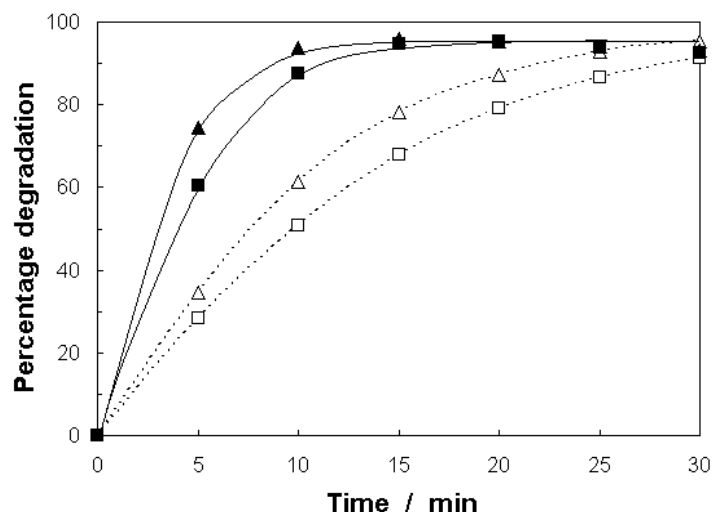
**Figure 4.** First order rate plot for the bleaching of 5 mg L<sup>-1</sup> Rhodamine B with 2% sodium hypochlorite.

Ultrasound intensity / W cm<sup>-2</sup>: □ 0 (no ultrasound) ◆ 1.5 ▲ 3.0 ■ 4.6 ● 6.7

Hypochlorite bleaches via the strongly oxidising OCl<sup>-</sup> ion which, in aqueous solution, is in equilibrium with hypochlorous acid, HOCl so that the reactions are pH dependent. The results shown above were measured with no pH control, the solutions being at the native pH of 11.7. Reactions conducted at pH < 7 (achieved by adding a small amount of aqueous HCl to the solution) were too fast to conveniently measure. Controlling the initial solution to pH 10 resulted in a small acceleration of the bleaching reaction over the unbuffered solution as shown in Figure 5. Lowering the pH of the solution will shift the equilibrium to form more hypochlorous acid, which is a strong oxidising agent in solution, resulting in a higher degradation rate. Behnajady and co-workers [25] showed that the rate bleaching of Rhodamine B solely using ultrasound was accelerated at low pH but that it was essentially constant above pH 6. Hence, the results shown here can be attributed to the effect of pH on the hypochlorite equilibrium.

The first-order rate constants are listed in Table 1. The rate constants are comparable with those reported in earlier literature [18, 25] although care must be taken in ensuring that the frequency, intensities and experimental conditions are similar. Higher rate constants have been reported at higher frequencies, corresponding to greater hydroxyl production, but consideration here has been confined to 20 kHz for comparison with the dental sources

described below. As expected, the reactions proceed faster with higher energy input. At the intensities involved here, the often observed point at which further rise gives no further increase in rate is not reached. It is clear that the rate of the sonochemical reaction is not simply the sum of the rate of the separate reactions in the absence of ultrasound and the absence of hypochlorite. The sonochemical acceleration may in part be due to local heating and enhanced mass transfer around cavitation bubbles but these would be expected to be small in comparison with chemical effects.



**Figure 5.** Effect of pH on the bleaching of 5 mg L<sup>-1</sup> Rhodamine B with 2% sodium hypochlorite solution. (Uncertainties in the percentage degradation are  $\pm 3\%$ )

No ultrasound:  $\blacksquare$  non-buffered;  $\triangle$  pH=10 :

Sonochemical reaction (6.7 W cm<sup>-2</sup>):  $\blacksquare$  non-buffered;  $\blacktriangle$  pH=10

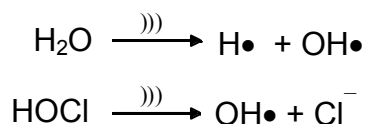
**Table 1.** Rate constants (min<sup>-1</sup>) for reaction of NaOCl with 5 mg L<sup>-1</sup> Rhodamine B

Ultrasound intensity / W cm <sup>-2</sup>	2% NaOCl unbuffered	2% NaOCl pH = 10	No NaOCl
0.0	0.082	0.105	0.0001
1.5	0.068	0.093	0.007
3.0	0.112	0.127	0.010
4.6	0.161	0.191	0.012
6.7	0.199	0.279	0.015

Concentration of NaOCl / wt%	Ultrasound 4.6 W cm <sup>-2</sup>	No ultrasound
0.5	0.081	0.032
1.0	0.129	0.058
1.5	0.129	0.068
2.0	0.170	0.081

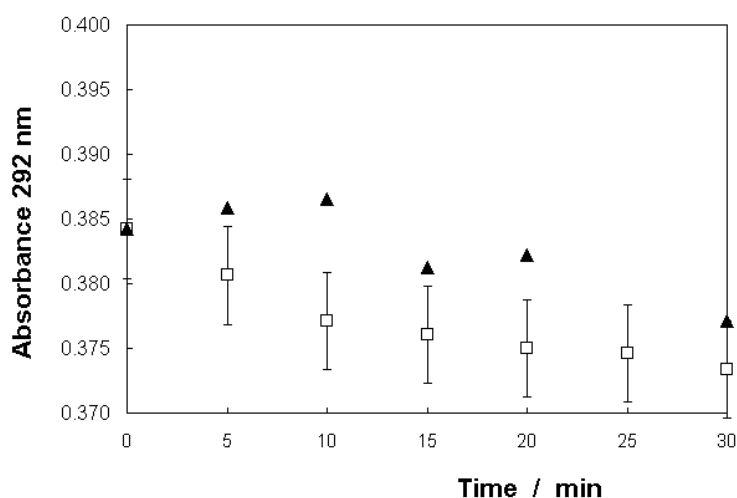


Sonolysis of water in the presence of ultrasound to produce hydroxyl radicals is a well known effect. [26] Undissociated hypochlorous acid could also evaporate into a cavitation bubble and undergo sonolysis, also (Scheme 1) producing  $\text{OH}\bullet$  radicals resulting in higher concentrations of these highly oxidising species, contributing to the acceleration of the degradation process. Zeng et. al. [27] also suggested that the presence of  $\text{HOCl}$  could result in the production of more hydroxyl radicals to accelerate the degradation of aqueous dyestuffs.



**Scheme 1.** Sonolysis of water and hypochlorous acid.

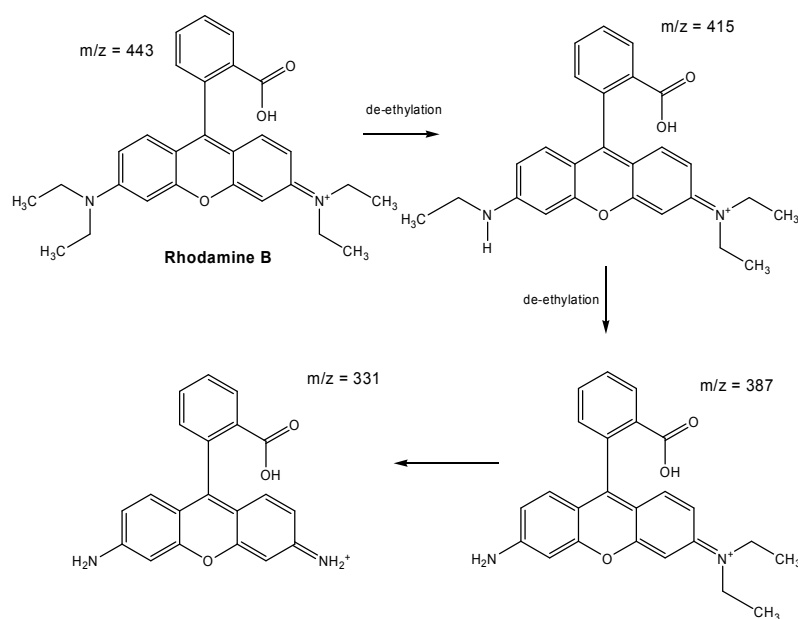
To further investigate the reasons for the acceleration, measurements of the concentration of  $\text{OCl}^-$  in solution were undertaken. The absorbance of a hypochlorite solution at 290 nm is mainly due to  $\text{OCl}^-$  ( $\epsilon_{\text{OCl}^-} \approx 350 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ;  $\epsilon_{\text{HOCl}} \approx 30 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ). [28] Rhodamine B loses colour when it reacts with  $\text{HOCl}$  and  $\text{OCl}^-$ . The concentration of  $\text{OCl}^-$  therefore falls during the reaction as shown in the absence of ultrasound in Figure 6. On the other hand, the absorbance of  $\text{OCl}^-$  fluctuates in the presence of ultrasound but remains higher than in the ‘silent’ reaction. The difference in concentration is  $\sim 1 \times 10^{-5} \text{ mol dm}^{-3}$  which, although small, is similar to the concentration of the dye. The  $\text{H}\bullet$  and  $\bullet\text{OH}$  radicals formed during sonolysis, will continuously react with the free chlorine and chloride present in the solution to form  $\text{OCl}^-$  and  $\text{HOCl}$  leading to higher concentrations and hence faster reactions.



**Figure 6.** Absorbance of  $\text{OCl}^-$  with respect to time at 290 nm.

□ without ultrasound ▲ with ultrasound  $4.6 \text{ W cm}^{-2}$

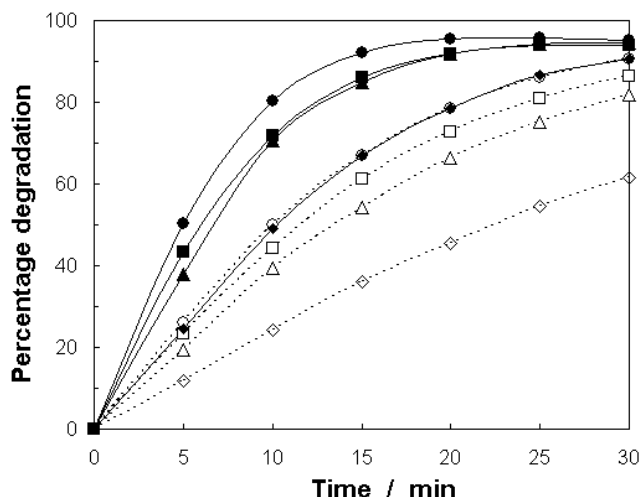
In order to better understand the reaction pathway, intermediate products formed were investigated using liquid chromatography coupled with mass spectrometry (LC/MS) for reactions conducted for 30 min with and without NaOCl. As noted above, in the absence of hypochlorite, the reaction is relatively slow and proceeds only to a limited extent. Here, the products detected were derivatives of Rhodamine B (Scheme 2) arising from deethylation processes. It should be noted that this represents only the very initial stages of the reaction as the intermediates represented will still contribute to the overall absorbance of the solution. The initial stages of the sonochemical reaction are therefore similar to those reported for catalysed photodegradations. [29-30] Even though the deethylation process can be seen clearly, cleavage of the chromophore of Rhodamine B also takes place at the same time, forming new compounds with lower molecular weights which were not detected in our system. An open system was used so that volatile products would be lost.



**Scheme 2.** Proposed reaction pathway of the initial degradation of Rhodamine B upon sonication, without NaOCl.

A more complex reaction mixture resulted when the solution was sonicated in the presence of NaOCl. As expected from the spectrophotometric results in Figure 2, only very small concentrations (e.g.  $\approx 0.2$  % w/v of the singly de-ethylated product with  $m/Z = 415$ ) remained after 30 min. A number of products with  $m/Z$  values in the range 226 – 301 were detected by unambiguous assignment of their structures was not possible.

The other major factor that influences the rate of this reaction is the concentration of hypochlorite. Figure 7 shows the degradation at fixed intensity and varying concentrations typical of those used in endodontics. The calculated first-order rate constants are listed in Table 1.



**Figure 7.** Effect of hypochlorite concentration on the bleaching of 5 mg L<sup>-1</sup> Rhodamine B  
 ◇, ◆ 0.5 %; △, ▲ 1.0 %; □, ■ 1.5 %; ○, ● 2.0 %. (Uncertainties in the percentage degradation are ± 3%)

Closed symbols - sonochemical reactions (4.6 W cm<sup>-2</sup>); open symbols – no ultrasound

A sonochemical acceleration was observed for each of the four concentrations investigated. The rate of reaction rises with increasing concentration. Significantly, the sonochemical reaction at 0.5 wt% hypochlorite gives a bleaching rate equivalent to 2 wt% in the absence of ultrasound. Both in sonochemical and dental applications of hypochlorite bleaching therefore, there will be benefit in using ultrasound to reduce the amount of NaOCl used. This adds to the benefit of ultrasound in “green” chemistry and also in enhancing patient safety in dental uses.

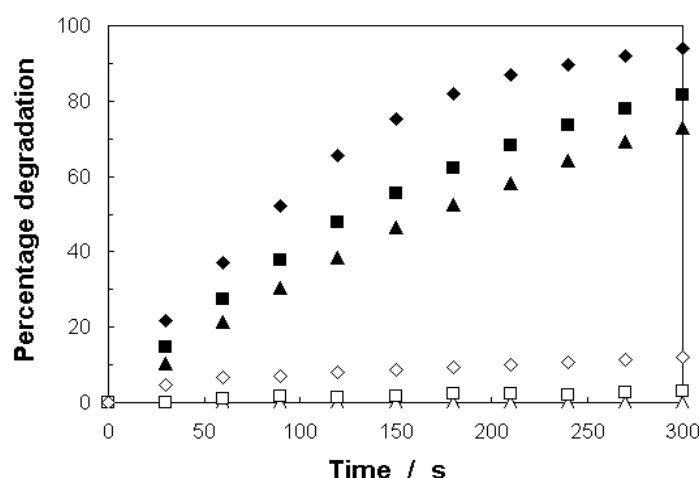
### 3.2 Endodontic sources

The role of the irrigant flow during root canal treatment on a tooth is to remove material from the cavity as well as to disinfect the root by killing diseased tissue. In addition to the physical effects of the flow, hypochlorite also promotes dissolution of debris by oxidation to more soluble products. Each of these processes will be promoted by the sonochemical effects referred to above.

Figure 8 shows that the same effects as observed on a sonochemical horn can be seen using the dental source. The results refer to Tip B from Figure 1. Even in the absence of

hypochlorite, bleaching of Rhodamine B occurs, albeit to a small degree. Around 12% of the dye is bleached after 5 min treatment at maximum power output. There is no reaction in the absence of ultrasound.

Addition of NaOCl degrades the dye rapidly even in the absence of ultrasound. However, using the ultrasonic instrument accelerates the reaction. For example, at the highest power, 2 min treatment results in a reduction of dye concentration of 65% compared with 38% in the absence of ultrasound. Thus, the reaction is accelerated by around 71% - or alternatively the same effect can be achieved with a 71% reduction in treatment time.



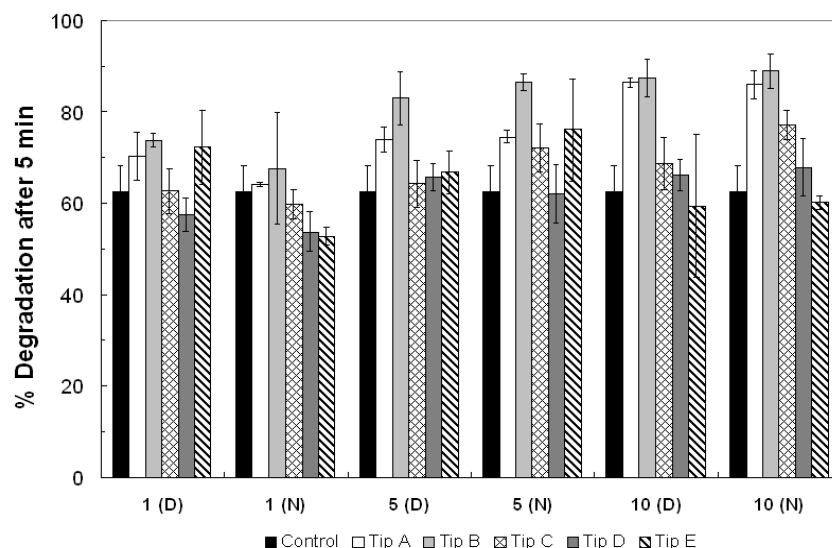
**Figure 8.** Bleaching of 5 mg L<sup>-1</sup> Rhodamine B using a dental endodontic system (Uncertainties in the Percentage degradation are  $\pm 4\%$ )

△, ▲ no ultrasound; □, ■ Setting 5; ◇, ◆ Setting 10

Closed symbols – 2.0 wt% NaOCl solution ; open symbols – no NaOCl

van der Sluis *et al.* [31] showed that the effectiveness of hypochlorite irrigants in removing debris from root canals depended on the design (for example the degree of taper) of the tip of an endodontic instrument. In addition, previous work with ultrasonic scaler instruments showed that their size and shape could affect both the amount and the spatial distribution of cavitation [4]. It was therefore of interest to investigate the bleaching reaction with tips with varying design.

Figure 9 shows the percentage of dye bleached after 5 min treatment for five tips at three power settings (1, 5 and 10). Each power has a ‘normal’ and ‘dry’ setting, where water flows through the cooling water tube from the handpiece towards the dental instrument on a ‘normal’ setting but not the latter. While there is some variation in the results, particularly at low power, some trends are clear.



**Figure 9.** Bleaching of 5 mg L<sup>-1</sup> Rhodamine B using a dental endodontic system with five different tips A – E (see Figure 1).

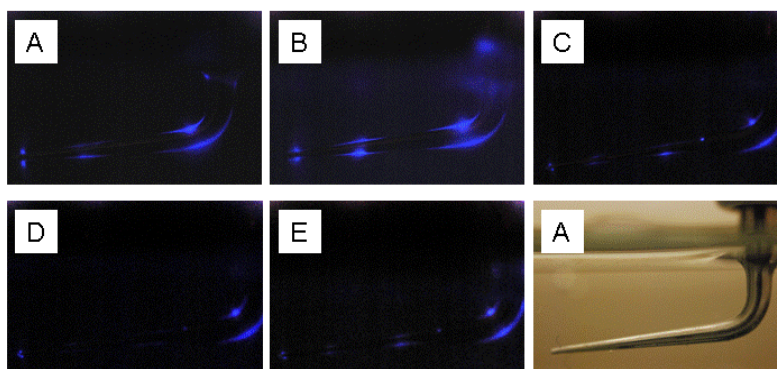
The key indicates the power setting and normal (N) or dry (D) settings. Control = no ultrasound. Error bars show the limits of replicate experiments.

For each setting, Tips A and B promote the largest effect in accelerating the bleaching with the latter being marginally more effective. Conversely, Tip D provides no benefit (within experimental uncertainty). Tips C and E are not very effective. These results have shown that the degradation rate is very much affected by the shape of the endodontic tips, which showed a close correlation to the total surface area throughout the working length of the tips. The surface area of each tip was estimated from 1:1 macro photography coupled with an image manipulation package in ImageJ. Another influence of the tip shape may be that the more effective tips are wider and hence higher pressures may be generated in the surrounding water during their motion, leading to higher numbers of cavitation bubbles being produced.

**Table 2.** Surface area, % decolourisation of Rhodamine B (5 min at power 10) and emission from luminol (30 s at power 10) for different dental tips

Tip	Surface area (cm <sup>2</sup> )	% Degradation (Rhodamine B)	Sonochemiluminescence emission intensity (a.u.)
Tip A	4.7	86	4.8
Tip B	4.9	87	5.7
Tip C	1.7	68	2.7
Tip D	1.8	67	2.7
Tip E	1.7	59	2.5

Based on the results in Table 2, it can be seen that tips that with larger surface area bleach Rhodamine B more effectively. In order to correlate these results with a sonochemical measurement, Figure 10 shows the distribution of luminol emission around each tip operating at full power while the total light emission, integrated over the same image area for each tip, is also shown in Table 2.



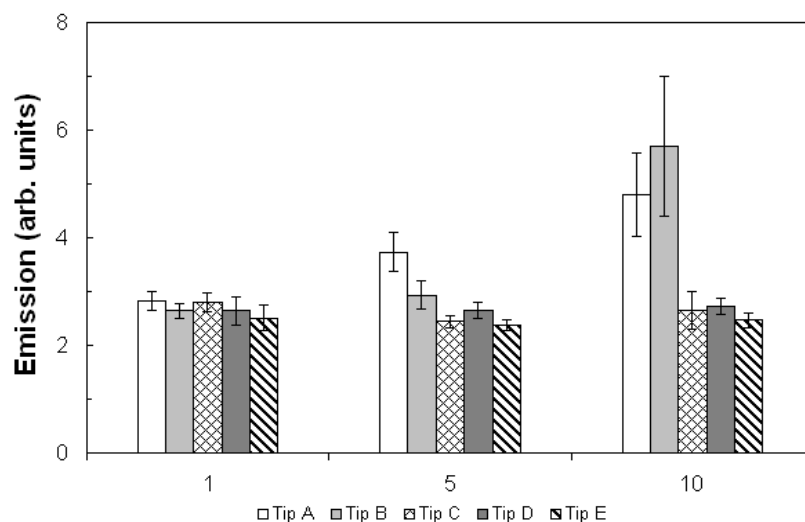
**Figure 10.** Luminol emission from endodontic instrument operating with different tips at power 10. The photograph of Tip A is included to show the orientation used.

The emission arises from reaction of sonochemically generated hydroxyl radicals with dissolved luminol. These results show that emission from A and B is brighter than with the other tips, agreeing with the dye bleaching results. The variation is connected with the pressure distributions emanated into solution when the tips vibrate. In order to allow a more quantitative comparison of the two series of experiments, the emission intensity was measured using image analysis software, the results being shown in Figure 11. Although the agreement is not perfect, it is clear that, particularly at the highest power, tips A and B give significantly higher emission than the other three, paralleling the bleaching rates. Further work is underway to provide a better quantitative comparison and explanation of the effect of tip shape on performance.

#### 4. Conclusions

The work has shown that the degradation of Rhodamine B is accelerated in the presence of ultrasound and that the reaction follows a *pseudo*-first order kinetics in the presence of NaOCl. Similar results have been obtained for the experiments performed using the endodontic instruments. The effectiveness of bleaching of Rhodamine B depends strongly on the surface area of the ultrasonic source – with endodontic tips of larger surface area

degrading higher percentage of Rhodamine B, and that can closely be related to the amount of sonoluminescence produced by each dental tip. Therefore, the bleaching of Rhodamine B with sodium hypochlorite can be used as an indicator of the sonochemical effectiveness of the dental tips in endodontic treatments.



**Figure 11.** Relative emission from luminol solutions using endodontic instrument operating at three powers (1, 5 and 10). The ‘normal’ settings with water flow through the handpiece were used. Error bars show the limits of replicate experiments.

### Acknowledgements

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